

One-Dimensional Single-Crystalline Mn₃O₄ Nanostructures with Tunable Length and Magnetic Properties of Mn₃O₄ Nanowires

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Experimental Details

Synthesis. All reagents and solvents were of analytical grade from commercial sources (Sigma-Aldrich) and used without further purification. Typically, 0.1–0.4 mmol of Mn(Ac)₃ (purchased from Aldrich) was dissolved in 32.5 mL of acetonitrile to form a red-brown solution. Afterwards, the solution was transferred to a 40 mL autoclave. To this solution was added 7.5 mL of a warm (50 °C) aqueous solution of aniline (2.25 mmol), which invokes the reaction mixture to become slightly turbid due to the hydrolysis of Mn(III) ions.^[35] The autoclave was sealed and maintained at 170 °C for 10 h and subsequently cooled to ambient temperature naturally. The as-prepared Mn₃O₄ nanowires are in the form of light orange sediments at the bottom of autoclave. Concomitantly, the polyaniline produced after oxidation polymerization is well dissolved in the solvent consisting of acetonitrile and water. Thus, the sediments (Mn₃O₄ nanowires) can be facilely separated by pouring off the supernatant polymer solution. The separated sediments were washed with ethanol for many times and dried. To examine the effect of solvent on the morphology of the nanostructured Mn₃O₄, 20, 10, and 2.5 mL of a warm (50 °C) aqueous solution of aniline (2.25 mmol) was added to 20, 30, and 37.5 mL of a Mn(Ac)₃ (0.2 mmol) solution in acetonitrile, respectively, while all the other experimental parameters remained unchanged. Likewise, light orange sediments were produced at the bottom of autoclave after the completion of the reaction.

Materials Characterization. Shape, size, and lattice structure of the Mn₃O₄ nanostructures were analyzed using a Hitachi S-4800 field-emission scanning electron microscopy (SEM), operated at 5 kV, a JEOL 1200 transmission electron microscopy (TEM), operated at 200 kV, or a FEI Tecnai G2 F20 S-Twin TEM, operated at 200 kV. The TEM specimens were prepared by dispersing the NW dispersions in ethanol onto ultrathin carbon-coated copper grids. The size distribution histograms of Mn₃O₄ nanowires were determined from the diameters of 300 nanowires found in enlarged microphotographs taken from several arbitrarily chosen areas on a copper grid. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-2400 diffractometer operated at 40 kV voltage and a 200 mA current with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). Magnetic studies were carried out on the nanowire powders using a MPMS2 Quantum Design SQUID magnetometer. Prior to magnetic measurements, the as-synthesized Mn₃O₄ nanowires were washed with a cosolvent of ethanol and acetonitrile (v/v = 1/1) for many times to thoroughly remove the adsorbed reactants and polyaniline.

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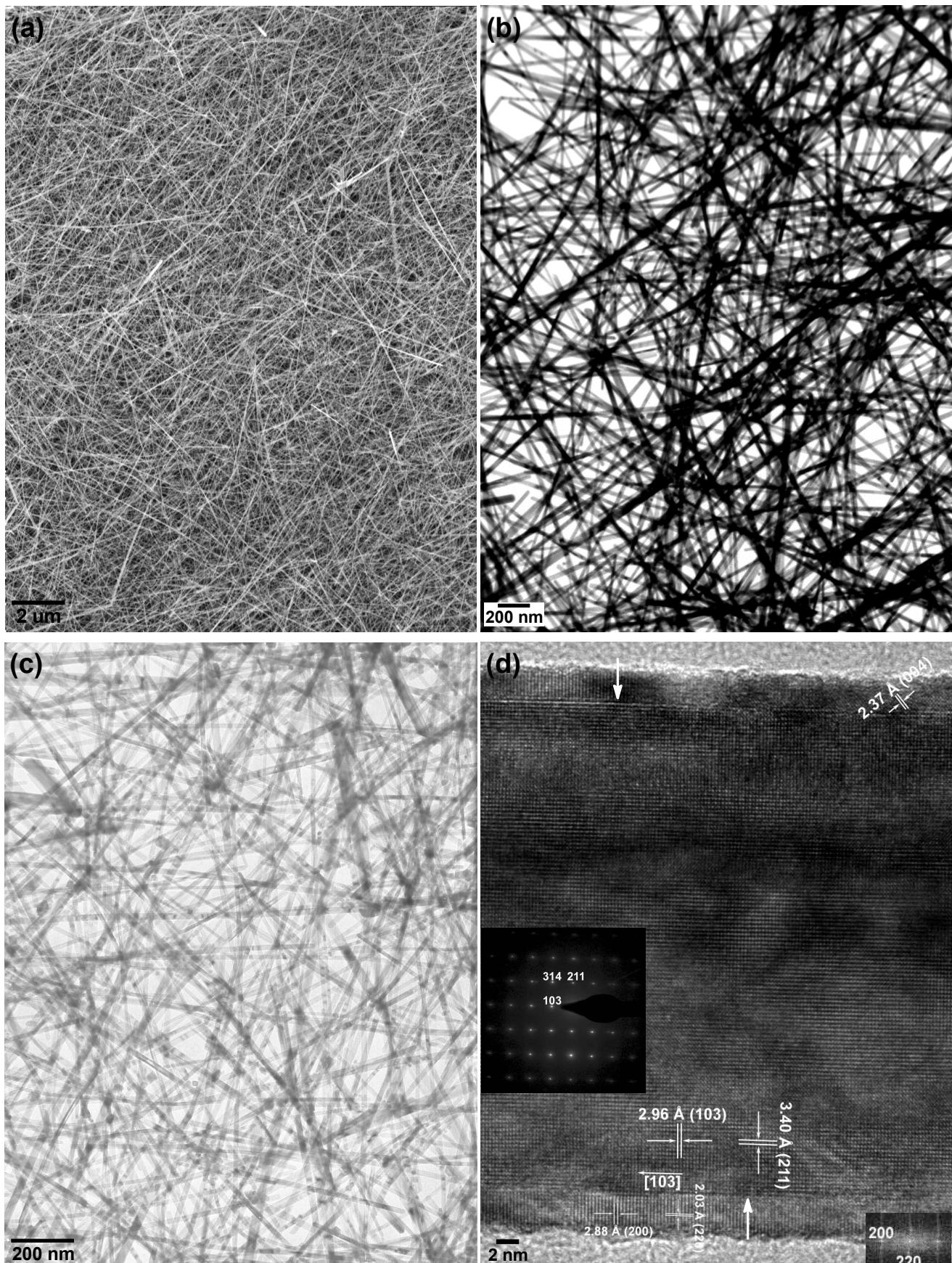


Figure S1. Additional SEM (a), TEM (b and c), and HRTEM (d) images of the Mn_3O_4 nanowires synthesized at a precursor $\text{Mn}(\text{Ac})_3$ concentration of (a, b) 5 mM, (c) 2.5 mM, and (d) 10 mM. The inset and arrows in panel d show the corresponding SAED pattern and a sharp interface, respectively. For the synthesis of Mn_3O_4 nanowires, the concentration of aniline is fixed at 56.25 mM, and the volume ratio of acetonitrile to H_2O is 32.5:7.5.

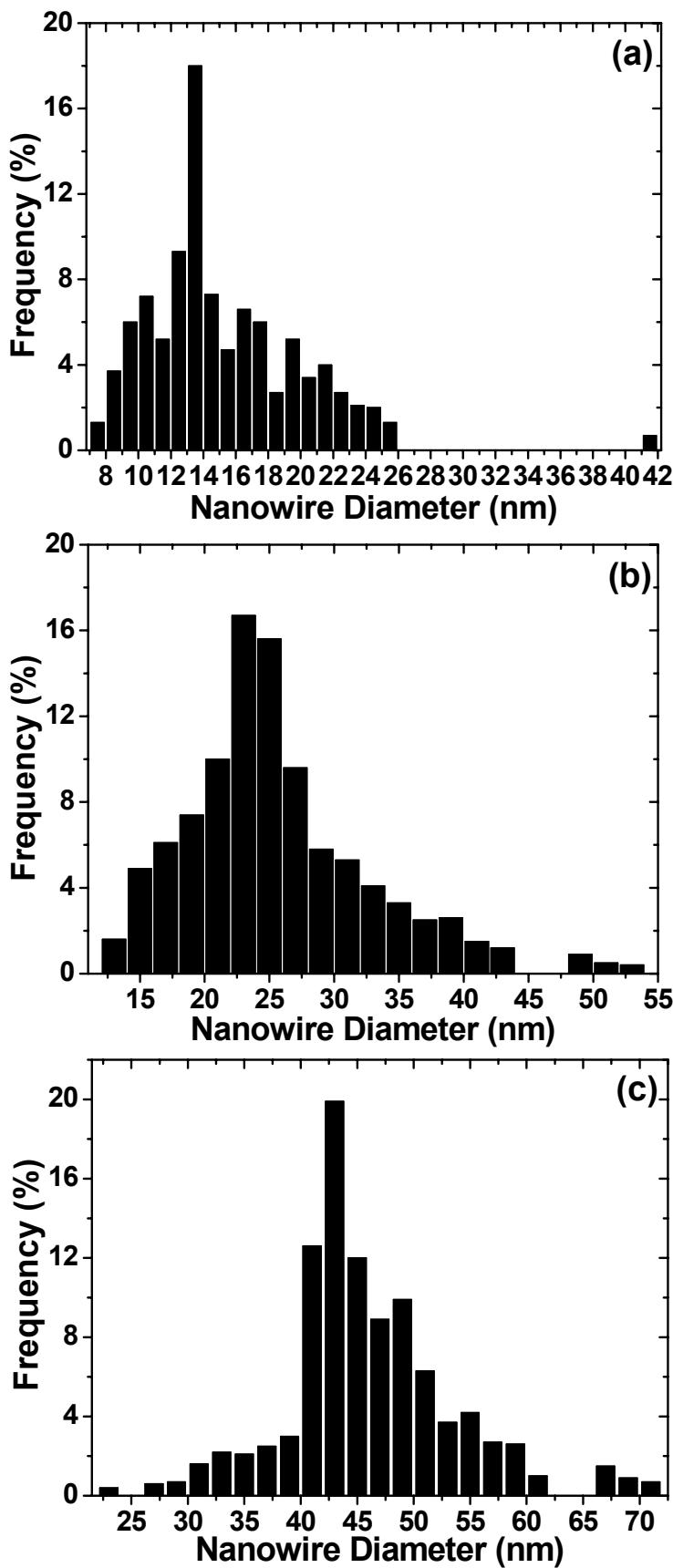


Figure S2. Diameter histograms of the Mn₃O₄ nanowires synthesized at a precursor Mn(Ac)₃ concentration of (a) 2.5 mM, (b) 5 mM, and (c) 10 mM.

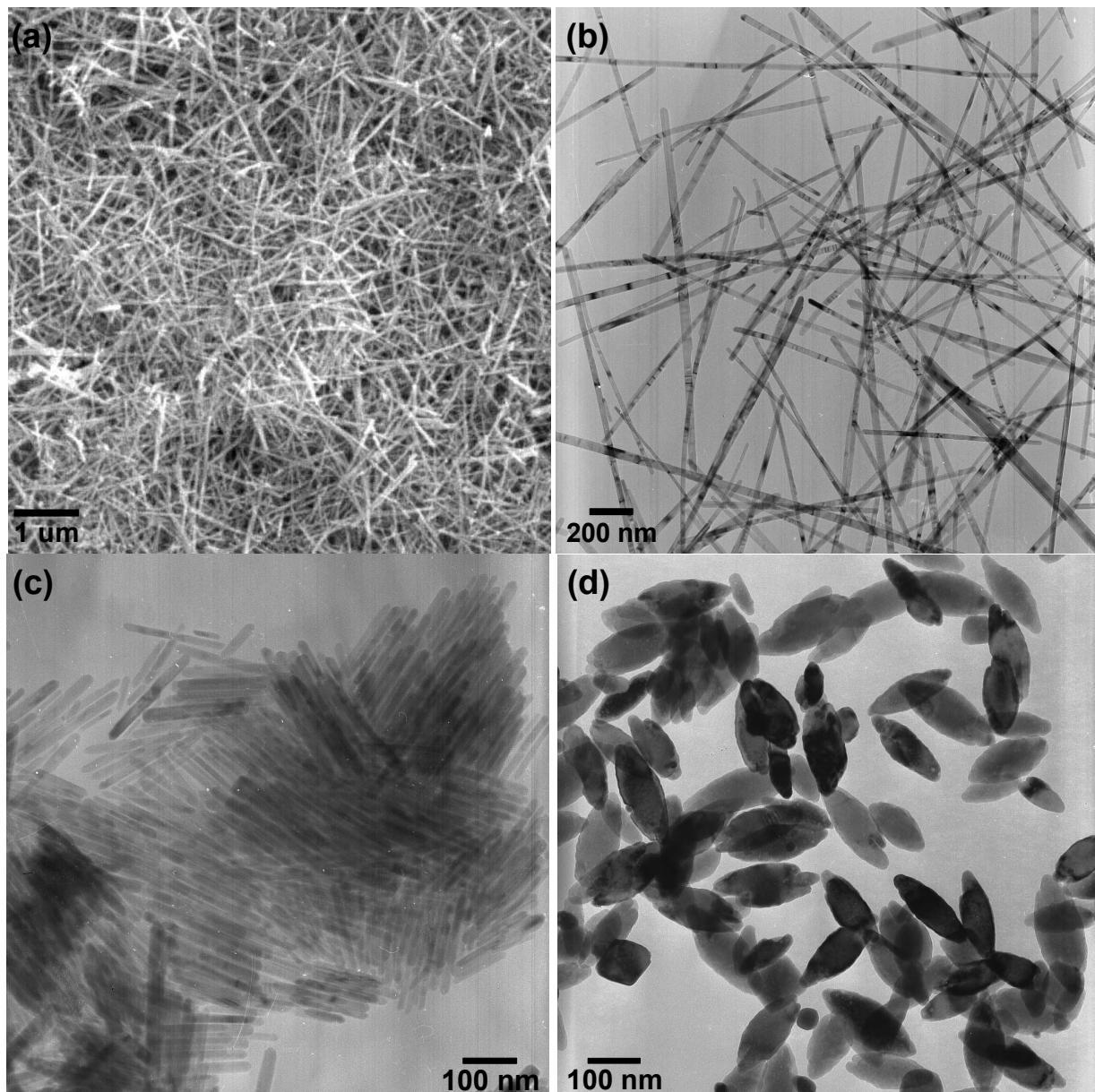


Figure S3. (a) SEM and (b) TEM images of short Mn₃O₄ nanowires, TEM images of (c) Mn₃O₄ nanorods and (d) olivary nanoparticles. The volumetric ratio of CH₃CN to H₂O in synthesis is (a) 3 : 1, (b) 1 : 1, and (c) 15 : 1, respectively. The amount of Mn(Ac)₃ is fixed at 0.2 mmol.